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Contact angles of selective wetting of hexylamine-modified silica surface

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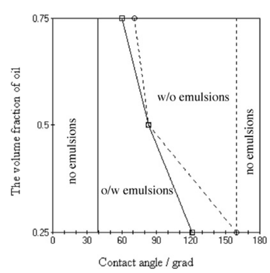
HIGHLIGHTS

- The angles of selective wetting of silica modified by hexylamine were measured.
- Modification of silica by hexylamine leads to inversion of the contact angle.
- The modification leads to phase inversion in the solid-stabilized-emulsions too.
- Empiric diagram of emulsion stability shows a region of complete instability.
- The emulsion type corresponded to the aqueous phase receding contact angle.

GRAPHICAL ABSTRACT



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ABSTRACT

It is shown experimentally that modification of silica particles by short-chain surfactant like hexylamine leads to inversion of selective wetting angle θ of the particles and to phase inversion in the emulsions stabilized by the hexylamine-modified silica particles. Empiric diagram of emulsion stability shows that at the contact angle θ close to 90° there is region of completely unstable emulsions between regions of stable emulsions of oil-in-water and water-in-oil types in the case of volume fraction of oil $\O_{oil} = 0.25$ or 0.75. At $\O_{oil} = 0.5$ the emulsion type and stability corresponded to the aqueous phase receding and advancing contact angles.

1. Introduction

Stabilization of emulsions by solid particles is determined by the following factors [1–17]: (1) the adsorption energy of a single particle on the interface; (2) forming of dense interfacial layer of the particles on the interface; (3) the capillary pressure in the emulsion film stabilized by solid particles; (4) mechanical strength and elasticity of the net-structure of the particles in the continuous phase.

These factors determining the emulsion type and stability depend on the contact angle θ of selective wetting of the solid particles [1–17]. As a result at the angle $\theta < 90°$ the oil in water emulsions (O/W) are formed, at the angle $\theta > 90°$ – the water in oil emulsion (W/O).

Modification by cationic surfactant is often used to increase the contact angle of surface of silica or glass. Molecules of cationic surfactant are chemically adsorbed at negative charge points that arise as a result of surface dissociation of silanol groups ≡Si—OH on surface of silica [18]. Long-chain surfactants (such as

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cetylthreemetylammonium bromide – CTAB, dodecylaminhydrochloride – DAHC) increase the contact angle θ to value about 85–90° for the oil–water interface (the equilibrium contact angle calculated by aqueous phase receding and advancing contact angles [12,19]) and to 40–70° for the water–air interface [20]. At further increasing of surfactant concentration the molecules of surfactant form second adsorbed layer orienting hydrophilic groups outside. Consequently the contact angle θ decreases again [12,20].

Accordingly the particles of CTAB-modified silica and of DAHC-modified milled glass stabilize only the O/W emulsions if volume ratio of oil and water was equal to 1:1 during preparation [12,19].

Modification of silica by hexylamine allows to obtain the W/O emulsions and to reach extremely hydrophobic particles when even the W/O emulsions became unstable [21,22].

In present work the contact angles of hexylamine-modified silica particles were investigated in the region of stable emulsions.

2. Materials and methods

2.1. Materials

Fumed silica particles (aerosil-380 with specific surface area 380 m^2/g and the particle diameter 12 nm) were used as solid stabilizer of emulsions. The particles of aerosil powder are aggregated always [18]. Radius of aggregates was calculated determined by characterized turbidity [23]:

$$[\tau] = \frac{\tau}{\lambda},$$

where τ is turbidity determined with photocolorimeter at light wavelength λ = 340; 400 and 590 nm. Average radius of aggregates was equal to 40 ± 5 nm.

Hexylamine (Merck) was used for modifying of silica surface.

Distilled water was used for preparing of aqueous solutions and dispersions.

Glass plate (with a thickness of 2 mm) and glass rod (with a diameter of 2 mm) modified by silica with hexylamine were used for measurement of the contact angles. Labor glass consists of about 70% of SiO_2 and silica particles precipitated on the glass surface forming thing layer.

Decane (Merck) was used as the oil phase.

2.2. Modifying of solid surface

The glass plate and rod were placed to the aqueous suspension of silica; hexylamine was added drop by drop with continuous stirring. Then suspension was stirred for a further 30 min. This process was followed by precipitation of silica particles on the glass surface and modifying its morphology. So the contact angles were measured on the silica layer fixed on the glass surface.

2.3. Preparation and characterization of the emulsions

The aqueous suspensions with concentration of hexylamine-modified silica $C_{SiO_2} = 1$–7% were used for preparation of the emulsion. The emulsions were prepared by shaking a tube with decane and aqueous suspension of hexylamine-modified silica at volume fraction of oil $\varnothing_{oil}$ = 0.25; 0.5 or 0.75. Stability of the emulsion was estimated by the life-time. The emulsion was considered to be stable if it was not destroyed in the gravity during 24 h.

2.4. Contact angles

Contact angles were measured on surface of a glass plate and rod that were modified by precipitation of silica particles at contact with suspension with concentration $C_{SiO_2} = 1\%$ or 5% and concentration of hexylamine C_{Hex} corresponded to the region of stable emulsions.

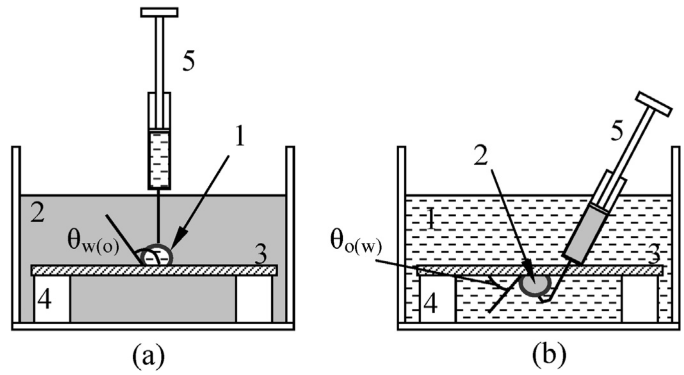

Fig. 1. The method of measurement of the static contact angle of a sessile drop of water in oil (a) and drop of oil in water (b) on the horizontal plate: 1 is aqueous phase, 2 is oil phase, 3 is the solid plate, 4 is support, 5 is syringe.

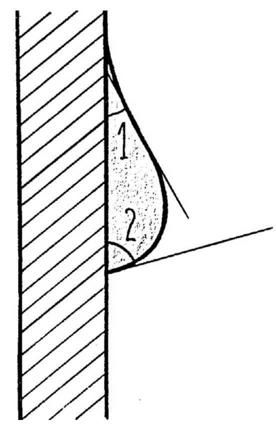

Fig. 2. The method of measurement of the water receding (1) and advancing (2) contact angles of a drop on the vertical surface.

Previously the glass surface was purified by a chromate mixture (solution of $K_2Cr_2O_7$ and H_2SO_4).

All measurements were carried out a day later at a room temperature about 25 °C. In all cases the contact angle was measured in the direction of the aqueous phase (Figs. 1 and 2).

The solution containing some amount of hexylamine equilibrium with adsorbed layer on the silica and glass surface (system of equilibrium aqueous solution-decane) or distilled water (system of water-decane) were used as the aqueous phase.

The static contact angle was measured by the sessile drop method on a horizontal glass plate (Fig. 1). With using syringe with needle a drop of the aqueous phase was placed to the upper side of the plate immersed in the oil. The contact angle of the aqueous phase drop in the oil phase $\theta_{w(o)}$ was measured toward the aqueous drop as it is shown in Fig. 1a.

A drop of the oil phase was placed by syringe with curve needle to the lower side of the plate immersed previously in the aqueous phase. The contact angle of the oil drop in the aqueous phase $\theta_{o(w)}$ was measured toward the aqueous phase too (Fig. 2b).

The drop was recorded with a photo camera. Diameter d of the base and height h of the drop were measured to calculate the contact angle. For the aqueous drop the contact angle is equal to

$$\theta = \mathrm{arctg}\frac{2hr}{h^2 - r^2} \quad \text{at } h > \frac{d}{2}, \tag{1}$$